

Spatial Structure of $4n\pi$ Helicene Dianions¹

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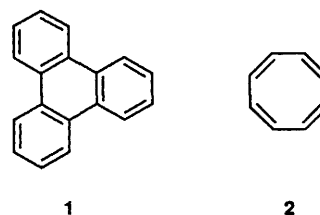
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Helicene dianions, *e.g.* phenanthrene derivatives, once believed to be non-helical, maintain their chirality as $4n\pi$ dianions. Phenanthrene **5**, as well as substituted phenanthrene derivatives, undergo a two-electron reduction to form the respective $4n\pi$ dianion *e.g.*, $5^{2-}/2Li^+$. Phenanthrene derivatives substituted at the 4- and 5-positions (bay substituents) *e.g.* **6–11**, which are helical, afford stable dianions. These dianions are also prepared by a two-electron reduction of the $(4n + 2)\pi$ electron hydrocarbons and show, in their ¹H NMR spectra, a quench of the paratropicity compared to 5^{2-} as well as a line shape dependence on their twist angle. The quench of paratropicity was also observed in the closely related charged helicenes derived from the benzo[*g*]chrysene system, *i.e.* anions 12^{2-} and 13^{2-} . The twist angles were calculated by MMX and MNDO calculations for the neutral systems, *i.e.*, **5–11**, and by MNDO for the dianions. MNDO calculations also included the preferred location of the counter cation. A dynamic NMR spectroscopic study proves experimentally the helicity of anion 11^{2-} thus shedding light on the behaviour of this novel class of dianions.

The study of charged systems has a twofold aspect: they can be used as model compounds for electronic theories and as reactive intermediates in organic chemistry.^{2–6} The most interesting and the least explored carbanion series are the $4n\pi$ electron dianions,⁷ entitled paratropic–antiaromatic. These $4n\pi$ polycyclic dianions are quite stable, and they have been studied mainly by NMR spectroscopy⁸ with respect to two major parameters: (a) the electronic structure as related to paratropicity, and (b) the detailed mode of electron delocalization. Intensive magnetic resonance studies performed on these dianions revealed some fundamental properties of antiaromatic charged systems.⁹ The $4n\pi$ systems are characterized by a narrow HOMO–LUMO energy gap (ΔE). Recently, this energy gap has been suggested as an index for the ¹H NMR paratropic shift of the $4n\pi$ polybenzenoid dianions on the one hand, and was shown to govern the line shapes in their ¹H NMR spectra on the other.^{9,10a,b} The polybenzenoid $4n\pi$ dianions seem to be the system of choice for examining the magnitude of the anisotropic paramagnetic susceptibilities, known to characterize $4n\pi$ cyclic conjugated systems, by means of their effect upon ¹H NMR chemical shifts. The rationale for linking the paratropicity and the line shapes is that antiaromaticity is a particular aspect of antibonding.¹¹ Thus the proximity of the excited antibonding states to the ground state, and consequently, the effect they exert upon it, is expected to be directly related to the antiaromatic character of the system.

HMO considerations differentiate between two classes of $(4n + 2)\pi$ -conjugated polycyclic species. Systems endowed with C_3 or higher axial symmetry for which the highest occupied and lowest unoccupied orbitals appear in pairs, and systems with lower axial symmetry in which no such orbital degeneracies exist.¹² The difference between the two classes becomes crucial when polycycles are reduced to the corresponding $4n\pi$ dianions. In the first group the two additional electrons populate two different degenerate orbitals, which lead either to a triplet ground state (*e.g.* triphenylene dianion¹³ **1**) or can stabilize the singlet state more than the triplet state by configuration interaction.¹² Systems with lower symmetry (*e.g.* anthracene, phenanthrene *etc.*) form, upon reduction, dianions in which the singlet state is lower in energy than the triplet state. It has been assumed that the rigidity, caused by the fused benzenoid skeleton, requires planar or near planar geometry and thus



reduces the extent of bond length alternation. These consequences stand in obvious contrast to $4n\pi$ monocyclic conjugated species, which reveal very large deviations from planarity¹⁴ (*e.g.* cyclooctatetraene **2**). As a result the HOMO–LUMO energy gap in the $4n\pi$ polycyclic dianions is much smaller than in the $4n\pi$ monocyclic systems.

Results and Discussion

The ¹H NMR spectra of $4n\pi$ polycyclic dianions are high-field shifted due to the charge effect as well as the paratropic effect.^{8–10} The extent of the paratropic shift beyond the charge effect can be taken as the 'pure' contribution of the antiaromatic paramagnetism. A good correlation was found between the calculated HOMO–LUMO energy gap (ΔE) of $4n\pi$ polycyclic dianions and the paratropic shift.^{9,10}

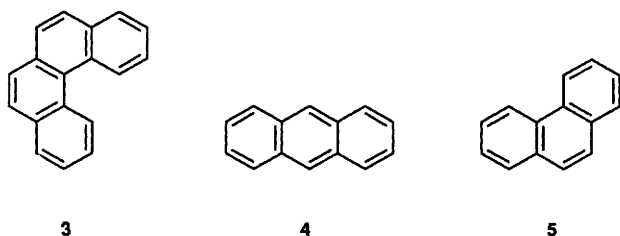
The paratropic ¹H NMR chemical shift is the outcome of the anisotropic paramagnetic field which is assumed to be sustained in $4n\pi$ antiaromatic cyclic or polycyclic conjugated systems. This field results, in turn, from a relatively large contribution of excited states to the ground state. Such a contribution was shown by Van Vleck to establish a positive, paramagnetic susceptibility.¹⁵ The efficiency of this process depends primarily upon the width of the splitting, between the lowest vacant and the highest occupied molecular orbitals—it increases as the gap decreases. Apart from this paratropic shift effect, there are also variations in the line shape of these $4n\pi$ polycyclic dianions. As already mentioned, dianions having C_3 or higher axial symmetry possess a ground triplet state and therefore show no NMR spectroscopic lines. However in dianions which belong to a lower symmetry group the singlet state is lower in energy than the triplet state, and since they are rigid, their HOMO–LUMO gap (ΔE) is very narrow (*vide infra*). It is obvious that in extreme

Table 1 'Antiaromaticity' and line shape spectral patterns and HOMO-LUMO energy gaps

Doubly charged systems	LUMO-HOMO gap (β units)	^1H NMR patterns ^a		
		30 °C	-20 °C	-60 °C
Tetracene-Li/THF	0.414	C	C	C
Tetracene-Na/THF		C	C	C
Anthracene-Li/THF	0.310	C	C	C
Anthracene-Na/THF		—	A	B
Anthracene-Na/THF-DME		B	C	C
Anthracene-K/THF		—	—	A
Chrysene-Li/THF	0.272	B	C	C
Chrysene-Na/THF		—	A	B
Phenanthrene-Li/THF	0.231	—	A	A
Phenanthrene-Li/THF-DME		—	A	B
Phenanthrene-Na/THF		—	—	—
1,2,3,4-Dibenzanthracene-Li/THF	0.157	—	—	—
1,2,3,4-Dibenzanthracene-Na/THF		—	—	—
3,4-Benzophenanthrene-Li/THF	0.111	—	—	—
3,4-Benzophenanthrene-Na/THF		—	—	—

^a (—) No spectra obtained. (A) Broad lines, unresolved structure. (B) Sharp lines, unresolved structure. (C) Sharp lines, fine resolved structure.

cases the HOMO-LUMO energy gap influences the line shape of the ^1H NMR spectra of $4n\pi$ polycyclic dianions. This observation was encountered in a series of $4n\pi$ electron polybenzenoid carbocyclic dianions and interpreted in terms of a triplet state involved in the ground state.^{9b} According to this hypothesis the line broadening observed in this series of charged systems arises from an equilibrium between a singlet and a low lying thermally accessible triplet state. The narrower the HOMO-LUMO energy gap (ΔE) the higher is the population of the triplet state. Thus it results in a paramagnetic dilution which is responsible for the shortening of the T_2 relaxation time and hence for the line broadening.¹⁶ This observation was made on the basis of the combined spectroscopic data (Table 1) where the doubly charged benzenoid systems were divided into three groups. The first group includes doubly charged species that reveal highly resolved ^1H NMR spectra independent of the reducing metal, solvent or temperature. The second group includes species that do not produce NMR spectroscopic lines irrespective of the experimental conditions (e.g. 3,4-benzophenanthrene dianion 3^{2-}). The third group includes species that show a dependency upon the counteranion, the solvent and the temperature⁹ (e.g., anthracene dianion 4^{2-} and phenanthrene dianion 5^{2-}). As can be seen from Table 1, there is a good correlation between the calculated HOMO-LUMO energy gap (ΔE) obtained from $\omega\beta$ -HMO calculations and the observed line broadening all along these subgroups.



From the above it can be concluded that the $4n\pi$ systems are characterized by a narrow HOMO-LUMO energy gap (ΔE) which is responsible for the paratropic shift and the line broadening of their ^1H NMR spectra. However, these $4n\pi$ polycyclic dianions were studied with respect to two parallel aspects: (a) the electronic structure as related to paratropicity, and (b) the detailed mode of electron delocalization. The correlation between the calculated HOMO-LUMO energy gap and the paratropicity as well as with the ^1H NMR line-shape

was studied without taking into account the different paths for delocalization of the various systems. Moreover, as already mentioned, the predicted increase of the paratropic character, in doubly charged $4n\pi$ polybenzenoids, is directly related to a marked decrease in geometric distortion, i.e. a deviation from planarity and severe bond length alternation, due to the rigidity of the system. Until now, no study has taken into account the effect of the potential nonplanarity of such systems on their spectroscopic parameters.

Our approach was to study a series of hydrocarbons and their double negatively charged derivatives, all of which have the same sp^2 skeleton and show a known degree of deviation from planarity (*vide infra*). We assume that the gross delocalization pattern in general, is the same as long as the sp^2 carbon skeleton is maintained. Thus, the relationship between the nonplanarity of the $4n\pi$ systems and the NMR spectroscopic parameters can be deduced. A system of choice for such a study is the charged $4n\pi$ helicene series. This series belongs to the C_2 point group and hence is chiral. It has been previously reported that such systems can be resolved into stable enantiomers if the barrier to racemization is sufficiently high.¹⁷ We chose to concentrate on alkyl substituted phenanthrenes, the smallest polycyclic molecules with an enforced helical structure,^{8,19} for two reasons: (a) it is possible to modify the twist angle of the phenanthrene by alkylation at the 4- and 5-positions; (b) phenanthrene dianion 5^{2-} displays an intermediate HOMO-LUMO energy gap resulting in significant dependency of its ^1H NMR line-shapes on the nature of the reducing metal, the temperature and the solvent (Table 1). The $4n\pi$ phenanthrene dianion displays an intermediate HOMO-LUMO energy gap.^{9b} Systems with narrower energy gaps do not show resolved ^1H NMR spectra because of the relatively high concentration of a thermally excited state. A wider energy gap will always give well-resolved ^1H NMR spectra, since thermal excitation to a triplet state is not possible. We believe that any minor change in the system's geometry and therefore in its energy gap, would give a significant change in the paratropicity and line shape of the ^1H NMR spectra. Moreover, phenanthrene dianion shows an EPR spectrum^{9b} which consisted of a sharp absorption at 1595 G in frozen solution of THF (tetrahydrofuran) at 150 K. This line is a low-field line assigned to the $M_s = 2$ transition of a thermally accessible excited triplet state,^{20,21} and serves as direct evidence for the possibility of thermal excitation of phenanthrene dianion. Therefore we assumed that changing the planarity of these systems will enable us to lower the amount of the triplet dianion.

Table 2 The influence of the spatial structure of $4n\pi$ polycyclic helicene dianions on their ^1H NMR spectra and calculated twist angle

Anion	$\delta_{9\text{-H},10\text{-H}}^a$		Proton line shapes ^b		Calcd twist angle (°)		NMR parameters ^{a,c}
	Hydrocarbon	Dianion	Na ⁺ counterion	Li ⁺ counterion	Hydrocarbon (MMX/MNDO)[8,7]	Anion (MNDO)[7]	
5^{2-}	7.83	-1.14	no spectrum	resolved -70 °C	0/2	19.87	0.62 (d, 2 H, 1- and 8-H, <i>J</i> 6.5) 0.80 (d, 2 H, 4- and 5-H, <i>J</i> 5.7) 1.69 (t, 2 H, 3- and 6-H, <i>J</i> 6.2) 2.75 (t, 2 H, 2- and 7-H, <i>J</i> 6.5) 2.40 (d, 2 H, 1- and 8-H, <i>J</i> 6.3) 3.62 (d, 2 H, 3- and 6-H, <i>J</i> 6.3) 4.32 (t, 2 H, 2- and 7-H, <i>J</i> 6.3)
6^{2-}	7.57	1.23	L.B. -20° resolved -70 °C	resolved +20 °C	33.02/36.86	58.82	2.74 (s, 2 H, 1- and 8-H) 3.71 (s, 2 H, 3- and 6-H) 0.65, 0.04 (s, 6 H, 6-H, Me) 2.87, 3.07 (s, 1 H, 1 H, 1- and 8-H) 4.15, 4.54 (s, 1 H, 1 H, 3- and 6-H) 1.23, 0.73 (s, 9 H, 9 H, Bu ^t) 1.42, 0.84 (s, 3 H, 3 H, Me) 0.40 (s, 3 H, Me)
7^{2-}	7.47	1.65	L.B. -20° resolved -70 °C	resolved +20 °C	33.15/—	—	0.42, 0.54 (d, 3 H, 3 H, Me, Pr ⁱ , <i>J</i> 3.9) 0.71, 1.48 (s, 3 H, 3 H, Me) 1.56, 1.65 (d, 1 H, 1 H, 1 H, 9- and 10-H, <i>J</i> 4.7) 4.18, 4.40 (d, 1 H, 1 H, 6- and 7-H, <i>J</i> 6.9) 4.59, 4.67 (d, 1 H, 1 H, 2- and 3-H, <i>J</i> 7.3)
10^{2-}	7.59d 7.87d (<i>J</i> 2 Hz)	2.49d 2.28d (<i>J</i> 2 Hz)	resolved -20 °C	resolved +20 °C	40.38/42.21	74.04	
11^{2-}	7.7-7.3m	1.56d (<i>J</i> 4.7 Hz)	L.B. -20 °C resolved -70 °C	resolved +20 °C	38.34/—	—	

^a NMR spectroscopic data for Li salts given in ppm relative to TMS; [$^2\text{H}_8$]-THF line at δ 3.67 taken as standard. ^b Line broadening: resolved = well resolved spectrum; L.B. = line broadening. ^c δ Values and coupling constants (*J* values in Hz) for the anions (9- and 10-H data not given).

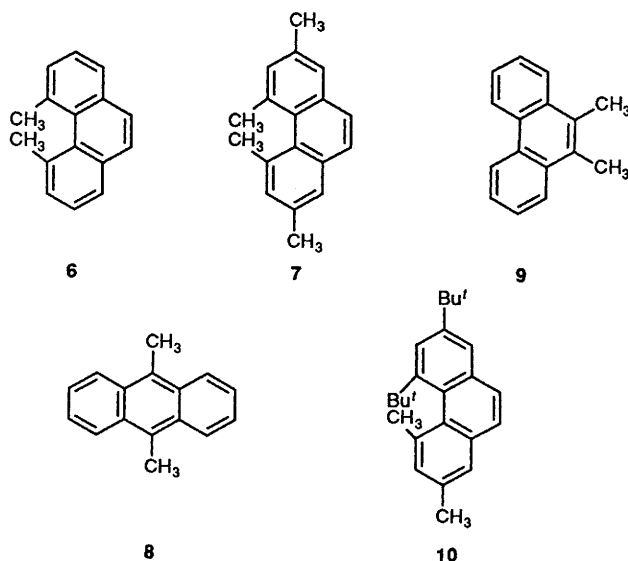
The reduction of a series of substituted phenanthrenes¹ was conducted with various different reducing alkali metals, and the NMR spectra of the charged products were studied at various temperatures. The structural features and energy levels of both the neutral and charged species were explored by the semi-empirical molecular orbital approach which relies extensively on Dewar's and Thiel's MNDO²² method. All internal degrees of freedom are relaxed during the geometry optimizations unless otherwise noted. All molecules are considered to exist as ground-state singlets. MNDO is an especially useful method for successfully predicting the structures of mono- and di-lithiated hydrocarbons,²² better by far than the $\omega\beta$ HMO calculations, which have been used for such studies, as they assume planarity in all the systems. Structural elucidation of the neutral species were carried out also by Molecular Mechanics calculations. This was done in order to recheck the MNDO's results since Molecular Mechanics is known to give very good structural predictions.

The twisting of the substituted phenanthrene systems was confirmed by ^1H NMR spectroscopic studies. The theoretical calculations are in good agreement with X-ray studies.¹⁹

The following effects were observed when 4- and 5-substituted phenanthrenes were reduced.

Line Broadening Effect.—On going from the almost planar unsubstituted phenanthrene dianion 5^{2-} to dianions substituted by bulky alkyl groups, the ^1H NMR line shapes become much narrower and fine structures can be observed (Table 2). Phenanthrene dianion 5^{2-} with sodium as counterion shows no ^1H NMR spectrum at temperatures as low as -70 °C. When lithium is the reducing metal, broad lines emerge at -20 °C. The spectrum is improved in terms of line shape as the temperature is further reduced. At -70 °C a well-resolved, easily interpretable NMR spectrum is observed. Twisting of the sp^2 framework of phenanthrene can be achieved by alkylation at the 4- and 5-positions, *i.e.* 4,5-dimethylphenanthrene **6**. Charging of this hydrocarbon leads to formation of the respective $4n\pi$ dianion and a significant narrowing in the line shapes is observed. When sodium was used as reducing metal to

the neutral $(4n + 2)\pi$ system **6**, broad lines at -20 °C are observed. At -70 °C a spectrum with rather narrow lines (although without observable spin-spin couplings) is obtained. The lithium salt of this dianion *i.e.* $6^{2-}/2\text{Li}^+$ shows a well-resolved spectrum even at room temperature. Similar results were obtained for 2,4,5,7-tetramethylphenanthrene dianion 7^{2-} in the same way that 9,10-dimethylanthracene dianion 8^{2-} resembles anthracene dianion 4^{2-} . From the similarity of behaviour of dianions obtained from **6** and **7** we conclude that the additional alkyl groups at positions other than 4 and 5 do not modify significantly the paratropicity and line-shapes of the anions. Moreover, 9,10-dimethylphenanthrene dianion $9^{2-}/2\text{Li}^+$ shows similar features to those of the parent anion, *i.e.* $5^{2-}/2\text{Li}^+$. This rules out the possibility that those line shapes are influenced by an electronic change in the molecule due to alkylation.



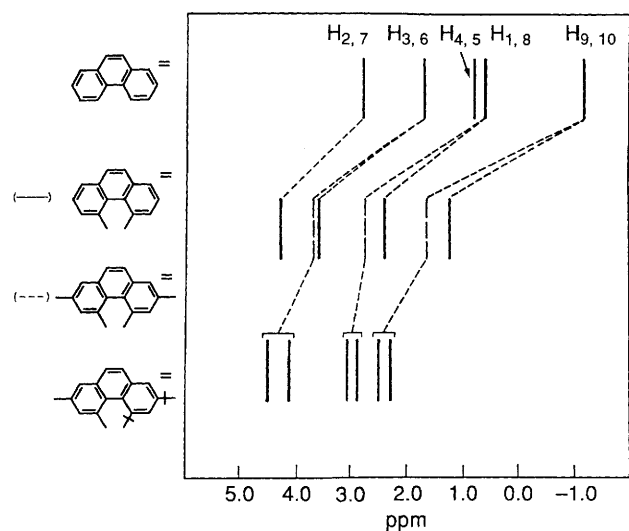


Fig. 1 ^1H NMR (200 MHz) chemical shifts of substituted phenanthrene dianions (as dilithium salts) represented by the stick diagram

Conversion of 2,4-di-*tert*-butyl-5,7-dimethylphenanthrene **10** to its dianion, resulted in an even more significant effect. Anion $10^{2-}/2\text{Na}^+$ already shows a resolved spectrum at -20°C , whereas, as expected, the lithium salt shows a very well resolved spectrum at room temperature. From all the above data we conclude that the more twisted is the helicene, the less significant becomes the line broadening.

Paratropicity.—The same trend is observed regarding the influence of the twisting of the helical sp^2 skeleton on the paratropicity of these $4n\pi$ systems. The more twisted is the helicene, the more quenched is the paratropicity of the $4n\pi$ system.¹ This phenomenon can clearly be seen in Fig. 1. In order to illustrate this phenomenon we applied the chemical shifts of the protons at positions 9 and 10 of the substituted phenanthrenes e.g. **6**, **7**, **8** and **10**, as probes. These positions have the largest charge density, as deduced from the NMR spectra and theoretical calculations. It can be seen that the high field shift is diminished as the twist angle becomes more pronounced (Table 2). The ^1H NMR spectroscopic lines of positions 9 and 10 of the phenanthrene dianion $5^{2-}/2\text{Li}^+$ are shifted to $\delta -1.14$, whereas the resonance of the same protons in the 2,4,5,7-tetramethylphenanthrene dianion $7^{2-}/2\text{Li}^+$ is shifted to $\delta +1.65$. Thus, a dramatic shift difference of 2.79 ppm results from the different paratropicities of these charged systems. In the more twisted moiety, i.e. 2,4-di-*tert*-butyl-5,7-dimethylphenanthrene dianion $10^{2-}/2\text{Li}^+$ the proton resonances of the same positions appear at $\delta 2.49$ and 2.28 respectively. The same trend is observed for the protons of the other positions (Table 2).

The origin of this phenomenon is attributed to the same source as the line broadening effect, i.e. the HOMO–LUMO energy gap of the dianions, and shows the same trend. This paratropic shift is an outcome of the term σ_{para} in the Ramsey equation^{23,24} (eqn. 1). In ^1H NMR spectroscopy this term is

$$\sigma_{para} = \frac{-e^2 h^2}{2m^2 c^2 \Delta E} \langle R^{-3} \rangle 2p \Sigma Q_{AB} \quad (1)$$

emphasized only when the excitation energy due to the HOMO–LUMO energy gap (ΔE) of the species is very small. This is the case in $4n\pi$ dianions, and therefore every change in this energy can be seen in the chemical shift. The wider is this energy gap, the less significant is the paramagnetic term in the total chemical

shift expression and hence the paratropicity of the system is quenched.

In all of the substituted phenanthrenes, the same charge distribution pattern has been observed. Changing the counterion or the temperature did not affect the observed trend of the line shapes and chemical shift differences. The paratropicity of $4n\pi$ ‘antiaromatic’ systems and the line shapes of their ^1H NMR spectroscopic signals thus correlate with the degree of twisting. Since antiaromaticity (as well as aromaticity) requires an efficient delocalization, twisting the system quenches its antiaromatic properties (i.e., the HOMO–LUMO energy gap gets wider).

Theoretical Calculations.—In the case of neutral species, structural characteristics were calculated using both molecular mechanics MMX force field method based on MM2 and MMPI programs developed by Allinger,²⁵ and Dewar’s and Thiel’s semi-empirical molecular orbital approach, MNDO method with some modifications. The structural results of the calculations obtained by the two methods of calculation were compared to each other and to literature X-ray crystallography results.¹⁹ As a parameter for the skeletal twist we consider the dihedral angle of the bay carbons i.e. C-4–C-4a–C-4b–C-5. The twist angle in the neutral species follows the same trend as the NMR parameters (*vide supra*). Unsubstituted phenanthrene **5** has a dihedral angle C-4–C-4a–C-4b–C-5 of 0° in the MMX method and 2° in the MNDO method. 4,5-Dimethylphenanthrene **6** shows a twist angle of 33.02° . Similar results are obtained for 2,4,5,7-tetramethylphenanthrene **7** (33.19°), which indicates, as shown by NMR spectroscopy, that the only substituents which are important for the observed different chemical shifts are those of the bay region (positions 4 and 5). 2,4-Di-*tert*-butyl-5,7-dimethylphenanthrene **10** shows a dihedral angle of 40.38° . Those species which have X-ray crystallography results¹⁹ are in good agreement with the calculated results, e.g. 4,5-dimethylphenanthrene **6** shows a dihedral angle between C-4–C-4a–C-4b–C-5 of 32° in its X-ray diffraction pattern and 33° as obtained by MMX calculations.

These results explain why we believe that the traditional $\omega\beta$ -HMO calculations which have been used so far for the study of $4n\pi$ polycyclic dianions do not afford a comprehensive description of the molecules. HMO calculations take for granted the planarity of the systems. This is also the reason for the inconsistency which we observed in our efforts to find a fit for the helicene series to the singlet–triplet equilibrium hypothesis. The only theoretical calculations which allow us to calculate such molecules and to get results as close to reality as possible is by exploring their multidimensional potential energy surfaces. We limit ourselves to a semiempirical molecular orbital approach for this problem as the size of the molecules precludes a rigorous *ab-initio* treatment. The MNDO method is an especially useful one for successfully predicting the structures of mono- and di-lithiated hydrocarbons.^{22,26}

The program used is the Molecular Theory Program Version 5.2.^{22b} The results obtained for the neutral species by this method are very similar to those obtained from the MMX program and from X-ray diffraction studies¹⁹ (Table 2). This program gives also the HOMO–LUMO energy gaps ca. 0.8 eV for all the neutral phenanthrenes.

When studying the $4n\pi$ charged species using the MNDO method, a new parameter is encountered, i.e., the position of the counteraction (the lithium cation). This location can modify the results and bring them to a local minimum. How sensitive and how close to reality those calculations are can be seen from the literature results of naphthalene dilithium and anthracene dilithium as compared to structures deduced from their X-ray diffraction.²⁷ Those species show, for different locations of the

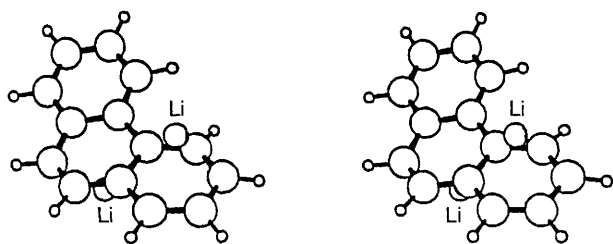


Fig. 2 Spatial structure of $5^{2-}/2Li^+$ obtained from MNDO calculations

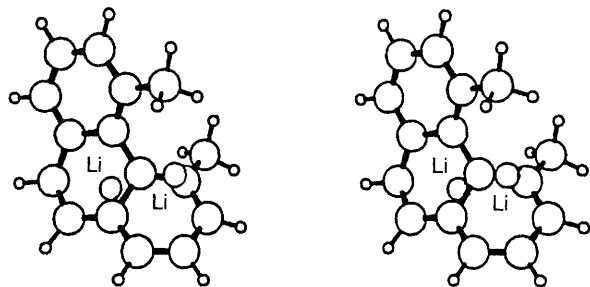


Fig. 3 Spatial structure of $6^{2-}/2Li^+$ obtained from MNDO calculations

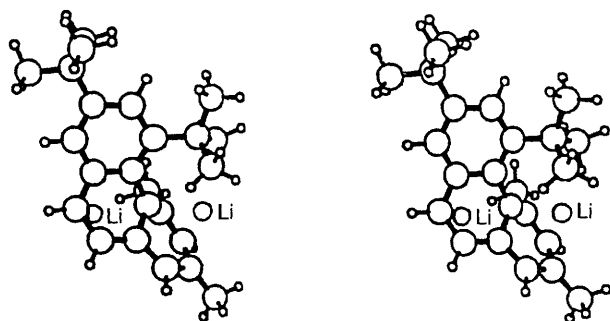


Fig. 4 Spatial structure of $10^{2-}/2Li^+$ obtained from MNDO calculations

counteranions, different local minima. However, the global minimum is in excellent agreement with the X-ray crystallography results reported by Stucky.^{27,28} In both cases the lowest energy arrangement was such that both lithium atoms bridge different rings on opposite faces. In a similar manner, we studied phenanthrene dilithium. It should be noted that all internal degrees of freedom are relaxed during the geometry optimization.

The unsubstituted phenanthrene dilithium, *i.e.* $5^{2-}/2Li^+$, shows in the MNDO calculation structural results which are analogous to those for anthracene and naphthalene dilithium salts. The counteranions are located in respect to the anion moiety of the phenanthrene plane so that they reside on opposite faces, one over the central ring and the other under one of the other rings. This arrangement showed the global energy minimum when compared to the other five possible locations of the counteranions and is in good agreement with the cation location reported by Rabideau.²⁸ However, in our studies, we obtained a lower energy of formation and a lower global minimum when the calculated species is not planar. This species shows a twist angle of the bay region of 19.87° , *i.e.* the dihedral angle between carbon atoms C-4-C-4a-C-4b-C-5 (Fig. 2). The same result of the global minimum is obtained whether we start from an input of a planar structure or an input of a twisted structure, *i.e.* a twist angle θ is either 0 or 30° . The fact that even the unsubstituted phenanthrene dianion which, in principle can

be planar without special steric hindrance is not planar, indicates that the antiaromatic species prefers a nonplanar structure in order to reduce its antiaromaticity. A more significant degree of twisting was calculated for the 4,5-dimethylphenanthrene dilithium salt $6^{2-}/2Li^+$. Again, in this case the most stable structure has the two lithium atoms facing the sp^2 phenanthrene moiety plane on opposite sides one above the central ring and the other below one of the other rings (Fig. 3). This arrangement affords an enthalpy of formation (ΔH_f) of $13.1 \text{ kcal mol}^{-1}$.^{*} Modifying the cation location affords less stable isomers. For example, displacement of the cation from the central ring to the 'empty' end affords enthalpy of formation of $17.43 \text{ kcal mol}^{-1}$. The twist angle obtained for this dianion is $\theta = 58.82^\circ$. The most pronounced degree of twisting is obtained for the 5,7-di-*tert*-butyl-2,4-dimethylphenanthrene dilithium $10^{2-}/2Li^+$. In this case, due to the nonsymmetry of the anion, additional possibilities for the location of the counteranion must be considered. The best results (most stable isomers) were those where one lithium is located above the ring bearing the methyl groups and the other lithium resides on the opposite face below the central ring (Fig. 4). The calculated enthalpy of formation for this species is $11.39 \text{ kcal mol}^{-1}$. The dihedral twist angle θ in this case is 74.04° .

As can be seen the $4n\pi$ phenanthrenes prefer a nonplanar spatial structure, in which the electron delocalization is perturbed and therefore the antiaromatic character of the species is quenched. These results correlate perfectly with the NMR spectroscopic data of the anions (*vide supra*). We have studied the influence of twisting upon the energy gap. Phenanthrene dilithium itself shows a calculated energy gap (ΔE) of 5.88 eV ($\theta = 19.87^\circ$). When we enforce a planar structure on this species the HOMO-LUMO energy gap (ΔE) becomes narrower. It indicates that deviation from planarity quenches the antiaromatic character of the $4n\pi$ helicene and hence changes the HOMO-LUMO energy gap. This can be rationalized since antiaromaticity is a property which requires an efficient cyclic electron delocalization of $4n\pi$ electrons in the same sense as aromaticity requires delocalization of $(4n + 2)\pi$ electrons as well as planarity which is one of the requirements for good delocalization. A nice example for this requirement is the cyclooctatetraene **2**, a nonaromatic $4n\pi$ conjugated cyclic hydrocarbon which loses its possible antiaromaticity by deviation from planarity, a structure which renders it to a simple conjugated polyene. In the case of the more highly twisted 4,5-dimethylphenanthrene dilithium $6^{2-}/2Li^+$ the energy gap is even wider, 5.96 eV (Table 2) and in the nonplanar 2,4-di-*tert*-butyl-5,7-dimethylphenanthrene dilithium $10^{2-}/2Li^+$, we find the widest gap of 6.0 eV .

We have also calculated the HOMO-LUMO energy gap (ΔE) of unsubstituted phenanthrene dilithium $5^{2-}/2Li^+$ while enforcing a twist angle of 58.82° upon its sp^2 skeleton in the bay region. This restriction caused an increase in the obtained HOMO-LUMO energy gap ($\Delta E = 6.09 \text{ eV}$). This result shows the importance of the dihedral angle θ in dictating the HOMO-LUMO energy gap in antiaromatic species.

Once again we see here that the trend of the increase in the HOMO-LUMO energy gap fits very nicely with the results discussed previously. We therefore conclude that two NMR parameters of $4n\pi$ antiaromatic systems are influenced by the spatial structure of the helicene dianions: (a) the paratropic shift of the system, and (b) the lineshape of their 1H NMR spectra. These 1H NMR parameters are governed by the HOMO-LUMO energy gap, and therefore they can be accepted as experimental probes for antiaromatic characterization.

* $1 \text{ cal} = 4.1868 \text{ J}$.

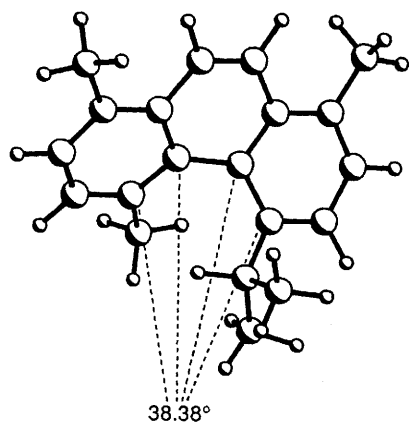


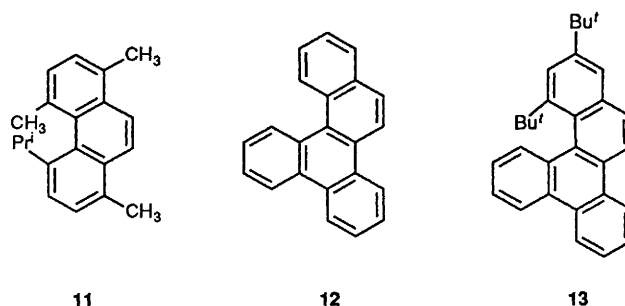
Fig. 5 Spatial structure of **11** obtained from molecular mechanics calculations

Dynamic NMR Spectroscopic Studies.—We have shown that the geometrical parameters of the parent helicene are modified as a result of the formation of the respective dianions. Our conclusions were based on theoretical calculations and the degree of paratropicity in the NMR spectra (Table 2). A comparison of the thermodynamic and kinetic parameters of the neutral systems with those of the anions would provide an insight into the changes which occur in the helicene system upon charging. We therefore synthesized the helicene 5-isopropyl-1,4,8-trimethylphenanthrene **11**.^{1b} This helicene has a stereochemical marker, *i.e.*, an isopropyl group in which the two methyl groups are diastereotopic. These sites interchange in the racemization process, due to a change in the sense of helicity. Therefore, in a slow racemization process, two separate ¹H NMR doublets for the two diastereotopic methyl groups are expected. Indeed, we see two doublets which appear at 1.6 and 0.56 ppm (*J* 6.6 Hz), respectively. The thermodynamic and kinetic parameters can therefore be deduced from dynamic NMR spectroscopic studies.^{29,30} The racemization process of **11** is very slow indeed (in the NMR time scale) and no significant changes in the proton spectrum can be observed up to a temperature of 435 K. We therefore resorted to the saturation transfer method. The advantage of this method over the normal (coalescence) ¹H NMR method is that the rates are compatible with $1/T_1$, and the measurements are carried out at relatively low temperatures. The experiment was carried out at 387 K by delivering a selective 180° pulse on the methyl line at 0.56 ppm, followed by a non-selective 90° pulse after increasing time delays (τ).³¹

The irradiation of one of the diastereotopic methyl groups affected the intensity of the ¹H NMR line of the other. From this dependency we calculated the rate constant for the racemization process.³¹ Introducing this rate constant into the Eyring equation gives ΔG^\ddagger value of 22.2 kcal mol⁻¹ for the racemization process. The calculated (MMX) twist angle θ of this neutral species is 38.34° (Fig. 5). Further Molecular Mechanics Calculations which were performed on this species show that a coplanar configuration of the bay region of **11** does not permit the methyl group at the 4-position and the isopropyl group at the 5-position to exchange positions; such a coplanar transition state requires a calculated free energy of *ca.* 36 kcal mol⁻¹. We therefore conclude that the transition state involves complex motions. The reduction product of **11**, *i.e.*, the 4nπ dianion **11**²⁻/2Li⁺ may undergo geometrical changes.³² This product has a new frontier orbital due to the filling of an antibonding orbital of the neutral system, a process which may result in elongation of carbon-carbon bonds. This dianion, *i.e.* **11**²⁻ can therefore either adopt a planar structure (allowing better delocalization) or a twisted structure (allowing a better

charge separation). The ¹H NMR spectrum points at a nonplanar asymmetric dianion, it shows a well resolved ¹H NMR spectrum of **11**²⁻ at room temperature due to its quenched paratropicity.

The two diastereotopic methyl groups show two separate doublets (0.42, 0.54 ppm, *J* 3.9 Hz). Elevating the temperature affords a coalescence at 319 K, and from the Gutowsky-Holm approximation²⁹ we could extract the rate constant for racemization. From the Eyring equation³⁰ the free energy barrier, ΔG^\ddagger for racemization of 15.4 kcal mol⁻¹ was obtained. We therefore conclude that the electronic structure induces changes in the dynamic behaviour of this nonplanar helicene dianion. It should be noted that despite the decreased barrier for racemization, the helicity of the dianion **11**²⁻/2Li⁺ is maintained.



We have also studied another twisted system which belongs to the helicene family. This group contains species with an sp² skeleton of benzo[*g*]chrysene **12**. Calculations ($\omega\beta$) predict a HOMO-LUMO energy gap (ΔE) of 0.165 β units for the dianion of benzo[*g*]chrysene, *i.e.*, **12**²⁻. Such an energy gap should, in principle, affect the ¹H NMR line broadening of this dianion to an extent in which a ¹H NMR line should not be detected. However, structural considerations (Molecular Mechanics) indicate that this neutral unsubstituted helicene is already twisted. Indeed, under low temperature conditions (225 K) the reduction product of **12** shows a well resolved ¹H NMR spectrum. The centre of gravity of the ¹H NMR spectrum of the potassium salt of **12**²⁻ is 3.36 ppm, a large paratropic shift indeed (Table 3).

A more twisted structure with the same sp² skeleton, *i.e.*, 12,14-di-*tert*-butylbenzo[*g*]chrysene **13** shows narrower ¹H NMR lines. The degree of twist of this sp² skeleton can be seen from MMX calculations. Under the same conditions the dianion of the substituted benzo[*g*]chrysene **13**²⁻/2K⁺ shows a well resolved spectrum already at 245 K. The lithium salt, *i.e.* **13**²⁻/2Li⁺ shows a well resolved spectrum already at room temperature (Table 3). As for the paratropicity, we see the same trend as seen for the substituted phenanthrene dianions (*vide supra*). The more twisted is the sp² moiety, the less paratropic the shift observed for the antiaromatic species. The 12,14-di-*tert*-butylbenzo[*g*]chrysene dianion (**13**²⁻/2K⁺) as potassium salt has a centre of gravity of its ¹H NMR shift of 4.65 ppm, *i.e.* *ca.* 1.3 ppm difference.

Conclusions.—We conclude that the paratropic ¹H NMR shift and the line broadening effect can serve as experimental parameters for assessing the degree of 'antiaromaticity' in 4nπ dianions. This study lends strength to the singlet triplet hypothesis and it emphasizes the effect of the planarity on their 'antiaromatic' characterization.

Experimental

NMR Spectra.—¹H and ¹³C NMR spectra were obtained with a Bruker WH-300 spectrometer, operating at 300.133 MHz

Table 3 ^1H NMR parameters of benzo[*g*]chrysene **12**, 12,14-di-*tert*-butylbenzo[*g*]chrysene **13** and their corresponding dianions

Compound	^1H NMR parameters ^a
12	8.98 (ddd, 1 H, 14-H, J_1 0.73, J_2 0.73, J_3 10.47) 8.94 (ddd, 1 H, 1-H, J_1 0.60, J_2 0.60, J_3 9.67) 8.82 (ddd, 1 H, 4-H, J_1 0.56, J_2 0.56, J_3 9.61) 8.79 (ddd, 1 H, 5-H, J_1 0.56, J_2 0.56, J_3 9.54) 8.75 (ddd, 1 H, 8-H, J_1 0.60, J_2 0.60, J_3 9.57) 8.70 (dd, 1 H, 9-H, J_1 0.61, J_2 8.98) 8.04 (ddd, 1 H, 11-H, J_1 0.57, J_2 0.57, J_3 9.52) 8.03 (ddd, 1 H, 10-H, J_1 0.60, J_2 0.71, J_3 8.89) 7.71 (ddd, 1 H, 7-H, J_1 2.54, J_2 6.94, J_3 6.94) 7.70 (ddd, 1 H, 3-H, J_1 2.02, J_2 6.81, J_3 9.57) 7.69 (ddd, 1 H, 6-H, J_1 2.63, J_2 6.66, J_3 6.66) 7.65 (ddd, 1 H, 2-H, J_1 1.77, J_2 6.98, J_3 7.91) 7.64 (ddd, 1 H, 13-H, J_1 1.47, J_2 6.87, J_3 7.75) 7.60 (ddd, 1 H, 12-H, J_1 1.47, J_2 6.87, J_3 7.75)
12²⁻/2K⁺	4.84 (t, 1 H, J 7.2); 4.69 (t, 1 H, J 5.5); 4.17 (t, 1 H, J 6.0); 3.97 (d, 1 H, J 7.2); 3.81 (t, 1 H, J 7.2); 3.73–3.58 (m, 4H); 3.46 (t, 1 H, J 5.5); 2.94 (d, 1 H, J 6.8); 2.25 (d, 1 H, J 6.8); 1.64 (d, 1 H, J 7.2); 0.96 (d, 1 H, J 7.3)
13	8.66 (ddd, 1 H, 5-H, J_1 8.7, J_2 1.2, J_3 0.9); 8.59 (d, 1 H, 8-H, J 0.56); 8.55 (d, 1 H, 4-H, J 0.6); 8.33 (d, 1 H, 9-H, J 8.5); 8.33 (d, 1 H, 9-H, J 8.5); 8.29 (ddd, 1 H, 1-H, J_1 8.15, J_2 1.4, J_3 0.5); 7.88 (s, 1 H, 13-H); 7.82 (d, 1 H, 10-H, J 0.5); 7.70 (d, 1 H, 7-H, J 8.9); 7.66 (dd, 1 H, 6-H, J_1 7.26, J_2 1.66); 7.62 (d, 1 H, 11-H, J 2.0); 7.54 (d, 1 H, 3-H, J 8.1); 7.44 (dd, 1 H, 2-H, J_1 6.9, J_2 1.3); 1.49 (s, 9 H, 12-Bu ^t); 1.00 (s, 9 H, 14-Bu ^t)
13²⁻/2Li	5.65 (t, 1 H, 7-H, J 7.29); 5.56 (td, 1 H, 6-H, J_1 5.5, J_2 1.1); 5.52 (dd, 1 H, 5-H, J_1 7.4, J_2 1.15); 5.42 (d, 1 H, 4-H, J 7.4); 5.32 (s, 1 H, 13-H); 5.12 (d, 1 H, 8-H, J 7.3); 5.06 (td, 2-H, J_1 6.91, J_2 1.2); 4.6 (d, 1 H, 1-H, J 8.64); 4.31 (t, 1 H, 3-H, J 8.2); 4.27 (s, 1 H, 11-H); 3.55 (d, 1 H, 9-H, J 6.1); 2.77 (d, 1 H, 10-H, J 6.1); 1.63 (s, 9 H, 14-Bu ^t); 0.88 (s, 9 H, 12-Bu ^t)

^a J values are given in Hz.

for protons, with a deuterium lock. All spectra are reported relative to Me₄Si. The ^1H NMR absorption of THF at 3.67 ppm was used for calibration. The assignments were assisted by 2D-NMR programs from the Bruker library DISN87. Some 2D-NMR spectra were recorded with the aid of a Bruker AMX-400 spectrometer operating at 400.14 MHz for proton equipped with an X-32 computer.

^1H NMR and saturation transfer experiments were performed on a Bruker WP-200 pulsed-FT spectrometer operating at 200.13 MHz for protons, equipped with pulse programmer and ^2H -lock systems, and an Aspect-2000 computer (82 K). M.p.s were obtained using a Thomas Hoover uni-melt capillary melting point apparatus.

Materials.—Products obtained by literature procedures gave satisfactory microanalyses and m.p.s. Helicenes were prepared *via* a Wittig reaction*³³ followed by a photochemical ring-closure reaction.³⁴ Wittig reactions of aldehydes and phosphonium salts were performed by the common organometallic procedures*³³ yielding crude alkenes which were purified by column chromatography on silica gel or neutral alumina. The mixture of *E*- and *Z*-1,2-diarylethenes was used directly for the photocyclization.

Wittig Reaction.—*General procedure.* (a) Substituted benzyl bromide (0.04 mol) and triphenylphosphine (0.04 mole) were

* The syntheses were performed according to the 'organometallic method' with BuLi (1.6 mol dm⁻³ in cyclohexane) as base and THF as solvent.

dissolved in *p*-cymene (60 cm³) (sometimes mesitylene or benzene) was refluxed for 2.5 h (mesitylene or benzene 12 h). The mixture was cooled, filtered and washed with light petroleum.

(b) The dry phosphonium salt (0.0025 mol) was dissolved in dry THF (distilled over potassium (50 cm³)). Butyl- or phenyllithium was added (0.003 mol) under an inert atmosphere and the mixture was stirred until it became red (or orange) and all the phosphonium salt had dissolved. The mixture was stood for another 2.0 h (if phosphonium salt remained undissolved, the mixture was refluxed gently).

(c) The aldehyde (0.005 mol) in dry THF (10 cm³) was then added dropwise while the reaction mixture cooled. The reaction mixture was stood for a further 12 h.

(d) The mixture was extracted with water, the solvent evaporated, and the product was purified by column chromatography on silica gel or neutral alumina to get the respective (*E*)- and (*Z*)-1,2-diarylethene.

The following starting materials for the Wittig reaction were purchased from Aldrich: 3-Methylbenzaldehyde, 3-methylbenzyl bromide and 2,5-dimethylbenzaldehyde.

Photocyclization of 1,2-Diarylethenes.—A quartz photo-reactor with forced water circulation, equipped with an unfiltered Hg high pressure lamp TQ150 was fitted into a pyrex cell containing the 1,2-diarylethene dissolved in distilled spectroscopic grade cyclohexane and some crystals of iodine. The course of the reaction was followed by TLC on silica gel. When the reaction was complete, the cyclohexane solution was washed with saturated aqueous Na₂S₂O₃ (100 cm³), dried (Na₂SO₄) and evaporated. The product was purified by column chromatography on silica gel or alumina, and sublimated. The yields range between 20 and 50%.

3,5-Dimethylbenzaldehyde, 3,5-di-*tert*-butylbenzaldehyde, 3,5-dimethylbenzyl bromide and 3,5-di-*tert*-butylbenzyl bromide were synthesized according to the literature.³⁴

Preparation of Phenanthrenes.—4,5-Dimethylphenanthrene **6** (m.p. 75 °C) was prepared by Wittig reaction*³³ of 3-methylbenzaldehyde and 3-methylbenzyl chloride (yield 10%), followed by photocyclization.³⁴

2,4,5,7-Tetramethylphenanthrene **7** (yield 35%; m.p. 112 °C) was prepared according to the literature^{33,34} from 3,5-dimethylbenzaldehyde and 3,5-dimethylbenzyl bromide.

2,4-Di-*tert*-butyl-5,7-dimethylphenanthrene **10** (yield 30%; m.p. 91 °C) was prepared according to literature^{33,34} from 3,5-dimethylbenzaldehyde and 3,5-di-*tert*-butylbenzyl bromide. ^1H NMR spectroscopic data is given in Table 2.

5-Isopropyl-1,4,8-trimethylphenanthrene **11** was prepared from 5-isopropyl-2-methylbenzyl chloride³⁵ and 2,5-dimethylbenzaldehyde according to the general procedure and purified by column chromatography on silica (light petroleum–methylene dichloride 80:20); m.p. 149 °C (Found: C, 91.48; H, 8.54. Calc. for C₂₀H₂₂: C, 91.55; H, 8.45%). *m/z* 262. ^1H NMR spectroscopic data is given in Table 2.

Benzo[*g*]chrysene **12** was prepared from commercial (Aldrich) phenanthrene-9-carbaldehyde and benzyl chloride.^{33,35} The ^1H NMR parameters are in full agreement with the literature data.³⁶ ^1H NMR spectroscopic data is given in Table 2.

12,14-Di-*tert*-butylbenzo[*g*]chrysene **13** was prepared from commercial phenanthrene-9-carbaldehyde (Aldrich) and 1,3-di-*tert*-butylbenzyl bromide,^{33,34} m.p. 180 °C (10%). All ^1H NMR spectroscopic data is given in Tables 1 and 2.

Preparation of Anions.—Lithium, sodium wire or potassium pieces were introduced into the upper part of an extended NMR tube containing the polycyclic compound (5 mg) dissolved in [$^2\text{H}_8$]-THF (Aldrich) (0.7 cm³). The frozen solution was

degassed and sealed under vacuum. The solution was brought in contact with the alkali metal by inverting the tube. Formation of the anion was detected by ^1H NMR spectroscopy of the diamagnetic species.

Calculations.—The MMX calculations were performed on an IBM AT compatible (SER-386C) with the 80386 micro-processor and math coprocessor CX 83D87 applying the PC-MODEL MMX calculations Serena Software, USA.

MNDO calculations were performed on a CDC Syber 180/855 running under NOS. 2.7.1 and NOS/VE 1.4.1 program.²²

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